

EUROPEAN PATENT SPECIFICATION

(45) Date of publication of the patent specification:
19.07.89

(51) Int. Cl.⁴: **C11D 1/722, C11D 3/39,**
C11D 17/00

(21) Application number: **86201867.8**

(22) Date of filing: **24.10.86**

(54) Non-aqueous built liquid detergent composition.

(30) Priority: **11.11.85 GB 852772**

(43) Date of publication of application:
16.06.87 Bulletin 87/25

(45) Publication of the grant of the patent:
19.07.89 Bulletin 89/29

(64) Designated Contracting States:
CH DE ES FR GB IT LI NL SE

(56) References cited:
EP-A- 0 014 980
EP-A- 0 030 096
EP-A- 0 120 533
DE-A- 2 810 703
FR-A- 1 551 810
GB-A- 1 172 931

(73) Proprietor: **UNILEVER NV, Burgemeester**
s'Jacobplein 1 P.O. Box 760, NL-3000 DK Rotterdam(NL)
(64) Designated Contracting States: **CH DE ES FR IT LI NL SE**

(73) Proprietor: **UNILEVER PLC, Unilever House Blackfriars**
P.O. Box 68, London EC4P 4BQ(GB)
(64) Designated Contracting States: **GB**

(72) Inventor: **Möhlmann, Willem Michael Maria,**
Korneljedreef 67, NL-3137 BS Vlaardingen(NL)
Inventor: **Rek, Johannes Henricus Maria,**
Coomhertstraat 96, NL-3132 GK Vlaardingen(NL)

(74) Representative: **Waldron, Robin Michael et al, Unilever**
PLC Patent Division P.O. Box 68 Unilever House
Blackfriars, London EC4P 4BQ(GB)

EP 0 225 654 B1

Note: Within nine months from the publication of the mention of the grant of the European patent, any person may give notice to the European Patent Office of opposition to the European patent granted. Notice of opposition shall be filed in a written reasoned statement. It shall not be deemed to have been filed until the opposition fee has been paid (Art. 99(1) European patent convention).

Description

The present invention relates to non-aqueous, built liquid (including pasty) detergent compositions of the kind comprising a builder and a nonionic detergent surfactant which consists of an organic hydrophobic group which has been condensed with propylene oxide and ethylene oxide in a molar ratio of propylene oxide to ethylene oxide of at least 1 : 17 but less than 2 : 1.

Such a composition is disclosed in European Patent Application EP-A 30 096. In non-aqueous built liquid compositions containing nonionic detergent surfactant, it is known in general for that surfactant to be any type within the class of alkylene oxide condensation products with alcohols, alkylphenols, amides and so on, e.g. according to the latter specification or vide our British Patent Specifications 1 205 711, 1 270 040 and 1 292 352.

It has now been found that the rate of dissolution may be significantly improved in comparison with built compositions containing other nonionic surfactants, thereby obviating to a significant extent, the use of non-aqueous solvents, if the nonionic detergent surfactant is a block adduct wherein the organic hydrophobic moiety has been condensed first with the ethylene oxide and then with the propylene oxide.

One nonionic detergent surfactant which is an alkoxyated block adduct comprising a hydrophobic moiety condensed first with ethylene oxide and then propylene oxide is disclosed alone and unbuilt in Example 1e of patent specification DE-A 2 810 703. The propylene oxide to ethylene oxide mole ratio is 4 : 15. However, that surfactant is indicated there as undesirable for incorporation in built liquid detergent products on grounds of detergency and solidification upon low temperature storage. Other block adducts wherein condensation has been effected first with ethylene oxide and then with propylene oxide are envisaged for use in detergent powders, according to the disclosure of patent specification EP-A 14 980.

In the compositions of the present invention, the organic hydrophobic group may for example be selected from C_8 - C_{18} alkylphenols, C_8 - C_{18} primary or secondary, linear or branched-chain alcohols, C_8 - C_{18} fatty acid amides and so on. However, the molar ratio of propylene oxide (PO) to ethylene oxide (EO) is critical; too low a PO/EO ratio does not offer an advantage, and too high a PO/EO ratio influences the solubility negatively. The molar ratio of PO to EO in the nonionic detergent surfactants of the invention should lie within the range of at least 1 : 17 but less than 2 : 1, preferably of 7 : 4 to 1 : 2.

The nonionic detergent surfactants of the invention should furthermore not form high viscosity liquid crystalline phases in the presence of water, and should have cloud points of above 5°C. Suitable examples of nonionic detergent surfactants of the invention are C_{13} - C_{15} primary alcohol, condensed with 7 moles of ethylene oxide and 4 moles of propylene oxide and C_{13} - C_{15} alcohol, condensed with 4.9 moles of ethylene oxide and 2.7 moles of propylene oxide. Preferably, the nonionic detergent surfactants of the invention are low-foaming.

Mixtures of nonionic detergent surfactants of the invention with other detergent surfactants, such as anionic, cationic or ampholytic detergent surfactants, and soaps may also be used. If such mixtures are used, the mixture must be water-free and liquid at room temperature.

Examples of suitable anionic detergent surfactants are alkali metal, ammonium or alkylolamine salts of alkylbenzene sulphonates having from 10 to 18 carbon atoms in the alkyl group, alkyl and alkylether sulphonates having from 10 to 24 carbon atoms in the alkyl group and from 1 to 5 ethylene oxide groups, olefin sulphonates prepared by sulphonation of C_{10} - C_{24} -olefins and subsequent neutralisation and hydrolysis of the sulphonation reaction product. Examples of cationic detergent surfactants are aliphatic or aromatic higher alkyl di(lower alkyl) ammonium halides and examples of soaps are the alkali metal salts of C_{12} - C_{24} fatty acids.

In general, the composition of the invention contains the nonionic detergent surfactant in an amount of at least 10% by weight of the total composition. The amount of nonionic detergent surfactant present in the composition may be as high as about 90%, but in most cases the practical amount will lie between 20 and 70% and preferably between 20 and 50% by weight of the composition.

The builder which is used according to the present invention may be either a preferably anhydrous inorganic builder or an organic builder. Suitable organic builders are the alkali metal salts of aminopolycarboxylic acids, such as ethylene diaminetetraacetic acid (EDTA), nitrilotriacetic acid (NTA), diethylenetriamine pentacetic acid (DEPTA), hydroxyethylaminodiacetic acid and the like; alkali metal salts of ethane hydroxyphosphonic acids, aminophosphonic acids and the like; polyelectrolytes such as alkali metal salts of hydrolysed copolymers of ethylene with maleic anhydride and alkali metal polyacrylates; alkali metal alkenylsuccinates and the like, and sodium phytate. Suitable inorganic builders are zeolites, the alkaline ortho-, poly-, pyro- and metaphosphates, silicates, borates, carbonates. Also mixtures of organic and inorganic builders may be used. The organic builders need not be anhydrous, but can be used in the hydrated form in which they are normally sold, for example NTA $1H_2O$, EDTA $2H_2O$.

The amount of builder present in the composition may be from 1 to 70% by weight of the composition. For most commercial purposes the amount of builder is from about 10% to about 60% by weight of the composition. The builder should have a particle size of less than 300 μm , preferably less than 200 μm .

The weight ratio of the nonionic detergent surfactant to builder should generally lie within the range of

10 : 1 and 1 : 4, and for most commercial purposes within the range of 4 : 1 to 1 : 4, the preferred ratio being about 1 : 2.

The liquid detergent composition of the invention is substantially anhydrous, by which is to be understood that the final composition should contain not more than 5%, and preferably less than 2% by weight of water; this does not include any water of hydration.

The stability behaviour of the products may be further improved by the incorporation of a few per cent of an emulsifier or a thixotropic agent, such as lauric diethanolamide, ethoxylated lanolin, sodium dioctyl sulphosuccinate.

The viscosity of the composition will vary, depending upon its constituents. In order to ensure that the composition may be poured satisfactorily, it is preferred that the viscosity should be in the range of from 100 to 3,000 m.Pas, although higher viscosities up to 60,000 m.Pas can be satisfactory. If desired, the viscosity of the composition may be adjusted by the addition of amounts of up to 20% of a thinning agent, for example ethyl alcohol, hexane, heptane, benzene, xylene, toluene, tetrahydrofuran, dimethyl sulphoxide.

The composition may furthermore contain other materials which are considered normal and desirable additives in detergent compositions. For instance, bleaching agents such as alkali metal perborates (either anhydrous or in one of their hydrate forms) may be incorporated in an amount of from about 5 to about 30% by weight of the composition. Without substantially modifying the fundamental characteristics of the compositions of the invention, there can furthermore be incorporated enzymes, such as amylases and proteases, lipases, colouring agents, fluorescers, bleaching agent precursors and activators, bleach stabilizers, perfumes, bactericides, soil suspending agents and corrosion-inhibitors.

In this respect, it has surprisingly been found that bleach precursors such as tetraacetylene diamine are more stable in the non-aqueous detergent compositions of the present invention than in non-aqueous liquid detergent compositions on the basis of nonionic detergents other than those according to the invention.

Optionally, suspending agents such as highly voluminous metal oxides and metalloid oxides such as silica may also be included in an amount of 1-5% by weight.

The invention is illustrated by the following Examples in which the percentages are by weight.

The rates of solution of the composition were measured by adding the non-aqueous liquid detergent at a concentration of 6.5 g/l to tapwater of room temperature under constant stirring (100 rpm) and measuring the conductivity of the resulting mixture. The time at which the conductivity does not change anymore is recorded as the dissolution time.

Example I

The following formulations with different nonionic detergent surfactants as specified in Table A were prepared, and their cloud point, liquid crystalline (L.C.) phase formation and dissolution time were measured. The following results were obtained:

	% by weight
nonionic detergent surfactant	50
anhydrous sodium triphosphate	27.5
anhydrous sodium carbonate	7.5
sodium perborate monohydrate	15.0

Table A

	nonionic detergent surfactant	mol EO/ mol PO	PO/EO ratio	Cloud point (°C)	L.C. phase	Dissolution time (min.)
5	C ₁₃ -C ₁₅ primary alcohol, condensed with	7.0/-	-	46	+	8
	C ₁₂ -C ₁₅ primary alcohol, condensed with	7.0/-	-	50	+	10
	C ₁₂ -C ₁₃ primary alcohol, condensed with	6.5/-	-	39	+	8
	C ₁₃ -C ₁₅ primary alcohol, condensed with	6.5/0.5	1:13	40	+	7
10	C ₁₃ -C ₁₅ primary alcohol, condensed with	7.0/4.0	1:1.75	32	-	2
	C ₁₃ -C ₁₅ primary alcohol, condensed with	4.9/2.7	1:1.81	35	-	1
	C ₁₃ -C ₁₅ primary alcohol, condensed with	2.0/4.0	2:1	0	-	10
15	EO = ethylene oxide PO = propylene oxide					

Example 2

20 Repeating Example 1, using a C₉-C₁₅ primary alcohol mixture having an overall PO/EO molar ratio of 1:1.6 (3.5 mol PO and 5.5 mol EO), with a cloud point of 31°C, and a C₉-C₁₅ primary alcohol mixture having an overall PO/EO molar ratio of 1:2.5 (2.3 mol PO and 5.7 mol EO), with a cloud point of 39°C, gave the following results:

- 25 1) no L.C. formation
2) dissolution time: total dissolution in 2, respectively 3 minutes.

Example 3

30 The following non-aqueous built liquid detergent was prepared:

Example 3

The following non-aqueous built liquid detergent was prepared:

	% by weight
35 nonionic detergent surfactant	38.6
glycerol triacetate	5.0
40 sodium triphosphate (anhydrous)	30.0
sodium carbonate (anhydrous)	4.0
sodium perborate monohydrate	13.4
sodium oxoborate	2.1
45 tetraacetylthylenediamine	4.0
sodium carboxymethylcellulose	1.0
ethylenediamine tetraacetate (sodium salt)	0.15
50 ethylenediamine tetra(methylenephosphonic) acid (sodium salt)	0.1
fluorescer	0.3
protease (Savinase® T-granulate)	0.6
perfume	0.25
55 highly voluminous silica	1.0

The following nonionic detergent surfactants were used.

- 60 A. C₁₃-C₁₅ primary alcohol, condensed with 4.9 moles EO and 2.7 moles PO,
B. C₉-C₁₁ primary alcohol, condensed with 4 moles EO and 1.5 moles PO,
C. C₉-C₁₁ primary alcohol, condensed with 5.5 moles EO and 0.5 moles PO, and
D. C₉-C₁₁ primary alcohol, condensed with 6 moles of EO.

65

The stability of tetraacetythylenediamine (TAED) in each of these formulations was assessed by iodometric titration of the TAED which was left in the compositions after storage for 12 weeks at 37°C.

The following results were obtained:

% TAED left in the non-aqueous liquid detergent after storage for 12 weeks at 37°C:

with A:	70%
with B:	60%
with C:	45%
with D:	30%

Claims

1. A non-aqueous, built liquid detergent composition comprising a builder and a nonionic detergent surfactant which consists of an organic compound containing a hydrophobic group which has been condensed with propylene oxide and ethylene oxide in a molar ratio of propylene oxide to ethylene oxide in the range of at least 1 : 17 but less than 2 : 1, characterised in that the nonionic detergent surfactant is a block adduct wherein the organic hydrophobic moiety has been condensed first with the ethylene oxide and then with the propylene oxide.
2. A composition according to claim 1, further characterised in that the molar ratio lies within the range of from 1 : 2 to 7 : 4.
3. A composition according to claim 1 or 2, further characterised in that the organic compound containing a hydrophobic group is a C₈-C₁₈ alkylphenol or a C₈-C₁₈ primary or secondary linear or branched-chain alcohol or a C₈-C₁₈ fatty acid amide.
4. A composition according to any one of claims 1-3, further characterised in that it contains an alkali metal perborate and a low temperature bleach activator.

Patentansprüche

1. Nicht-wäßrige, aufgebaute, flüssige Reinigungsmittelzusammensetzung umfassend einen Gerüststoff und ein nicht-ionisches Reinigungsmittel-Tensid, das besteht aus einer organischen Verbindung, enthaltend eine hydrophobe Gruppe, die mit Propylenoxyd und Ethylenoxyd in einem molaren Verhältnis von Propylenoxyd zu Ethylenoxyd in dem Verhältnis von mindestens 1 : 17 aber weniger als 2 : 1 kondensiert worden ist, dadurch gekennzeichnet, daß das nicht-ionische Reinigungsmittel-Tensid ein Blockaddukt ist, worin der organische, hydrophobe Anteil zuerst mit dem Ethylenoxyd und dann mit dem Propylenoxyd kondensiert worden ist.
2. Zusammensetzung nach Anspruch 1, weiterhin dadurch gekennzeichnet, daß das molare Verhältnis innerhalb des Bereiches von 1 : 2 bis 7 : 4 liegt.
3. Zusammensetzung nach Anspruch 1 oder 2, weiterhin dadurch gekennzeichnet, daß die organische Verbindung, enthaltend eine hydrophobe Gruppe ein C₈-C₁₈-Alkylphenol oder ein C₈-C₁₈ primärer oder sekundärer, linearer oder verzweigt-kettiger Alkohol oder ein C₈-C₁₈-Fettsäureamid ist.
4. Zusammensetzung nach einem der Ansprüche 1-3, weiterhin dadurch gekennzeichnet, daß sie ein Alkalimetallperborat und einen Niedertemperatur-Bleichaktivator enthält.

Revendications

1. Composition détergente liquide non aqueuse à adjuvant actif, comprenant un adjuvant et un tensioactif détergent non ionique qui est constitué d'un composé organique contenant un groupe hydrophobe ayant été condensé avec de l'oxyde de propylène et de l'oxyde d'éthylène, dans un rapport molaire oxyde de propylène/oxyde d'éthylène dans la gamme d'au moins 1 : 17 mais de moins de 2 : 1, caractérisé en ce que le tensioactif détergent non ionique est un composé d'addition séquentiel dans lequel le groupe hydrophobe organique a été condensé d'abord avec l'oxyde d'éthylène, puis avec l'oxyde de propylène.
2. Composition selon la revendication 1, caractérisée en outre en ce que le rapport molaire se trouve dans la gamme de 1 : 2 à 7 : 4.
3. Composition selon la revendication 1 ou 2, caractérisée en outre en ce que le composé organique contenant un groupe hydrophobe est un alkyl(en C₈-C₁₈)phénol ou un alcool primaire ou secondaire en C₈-C₁₈, à chaîne linéaire ou ramifiée, ou un amide d'acide gras en C₈-C₁₈.
4. Composition selon l'une quelconque des revendications 1-3, caractérisée en outre en ce qu'elle contient un perborate de métal alcalin et un activateur de blanchiment basse température.